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(54) Title: PROCESS FOR MANUFACTURING A SILICOALUMINOPHOSPHATE MOLECULAR SIEVE

(57) Abstract: Small particle size SAPO-34 is obtained by using a tetraalkyl orthosilicate as the silicon source.



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PROCESS FOR MANUFACTURING A SILICOALUMINO-  
PHOSPHATE MOLECULAR SIEVE

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This invention relates to molecular sieves and processes for their manufacture. More especially it relates to the preparation of synthesis mixtures to control product characteristics. The invention relates especially to the manufacture of silicoaluminophosphate molecular sieves, and more especially SAPO-34.

In U.S. Patent No. 4 440 871, the preparation of a number of phosphorus-containing molecular sieves is described.

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The patent particularly describes processes for the manufacture of numerous crystalline microporous silicoaluminophosphates (SAPO's) including SAPO-34, employing sources of silicon (e.g., a silica sol), aluminium (e.g., hydrated aluminium oxide), and phosphorus (e.g., orthophosphoric acid), and an organic template, for example tetraethylammonium hydroxide (TEAOH), isopropylamine (iPrNH<sub>2</sub>) or di-n-propylamine (DPA). The patent, the disclosure of which is incorporated by reference herein, gives X-ray diffraction data for the SAPO's and describes their utilities in catalysis and absorption.

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International Application WO 00/06493 describes obtaining phosphorus-containing molecular sieves of lower particle size and narrower size distribution by agitation, e.g., stirring or tumbling.

EP-A-541 915 is concerned with the conversion of methanol to olefins (MTO), especially light (C<sub>2</sub> to C<sub>4</sub>) olefins, using an aluminophosphate crystalline

molecular sieve catalyst. The specification describes the advantages of small particle size catalysts in MTO processes, and provides a process for facilitating the manufacture of a small particle size material by stirring the synthesis mixture, producing SAPO-34 of median particle diameters, expressed as a mass distribution, in the range of about 0.6 to 1.4  $\mu\text{m}$ .

EP-A-185 525 describes a process in which SAPO-37 is manufactured using a two-phase synthesis mixture. In an example there are used an aqueous phase containing phosphoric acid, alumina, and tetraethyl and tetrapropyl ammonium hydroxides as organic templates, and an organic phase comprising tetraethyl orthosilicate in hexanol, a solvent immiscible with water.

International Application WO 01/36328 describes a process in which a SAPO-34 molecular sieve is manufactured in the form of isocrystalline spheroidal particles of from 0.5 to 30  $\mu\text{m}$  diameter using an aqueous synthesis mixture comprising a template, sources of the elements essential to the structure of the sieve and an organic solvent miscible with water, the purpose of the solvent being to solubilize the source of the silicon in the aqueous synthesis mixture, and a surfactant as morphology modifying agent. The silicon source may be a tetraalkyl orthosilicate.

The spheroidal particles of SAPO-34 are said to have a textured surface formed by crystallites the width (largest dimension) of which is from about 0.05 to 2.5  $\mu\text{m}$ , as determined by scanning electron microscopy. Although it is stated that reducing the concentration of silicon in the synthesis mixture

reduced the diameter of the spheroids, the product of the SAPO-34 examples is always spheroidal.

There remains a need, however, for a method whereby very small individual crystallites of SAPO-34 can be manufactured, as opposed to the clusters  
5 resulting from the process described in WO 01/36328.

It has now been found that by omitting the surfactant a SAPO-34 product in the form of individual crystallites of much reduced particle size may be  
10 obtained.

The present invention accordingly provides a process for the manufacture of a SAPO-34 crystalline molecular sieve which comprises forming a surfactant-free synthesis mixture containing sources of silicon,  
15 of aluminium, and of phosphorus, in proportions appropriate to the formation of SAPO-34, and a structure-directing agent, the source of silica being a tetraalkyl orthosilicate, and subjecting the synthesis mixture to hydrothermal treatment.

Advantageously, the molar ratio of silicon to aluminium, expressed as  $\text{SiO}_2 : \text{Al}_2\text{O}_3$ , is at most 0.5:1, since molar ratios higher than 0.5:1 are believed to contribute to the formation of a spheroidal particle as  
20 described in

WO 01/36328.

The invention also provides SAPO-34, the mean particle size of which is at most 400 nm, advantageously at most 200 nm, preferably at most 100 nm and most preferably at most 50 nm. The SAPO-34 is  
30 advantageously one obtainable by, and preferably is obtained by, the process of the invention. Mean particle size may be measured by inspection of scanning

electron micrographs (SEM's), the largest dimension of each particle being taken. Alternatively, particle size measurement may be carried out by XRD peak width analysis as described in certain of the Examples below.

5           The components of the synthesis mixture used in the present invention are typically those known in the art or as described in the literature as suitable for the production of SAPO-34, as are the conditions of the hydrothermal treatment, except for the essential use of  
10 a tetraalkyl orthosilicate as the silicon source, the absence of surfactant and/or the required ratio of  $\text{Al}_2\text{O}_3$  :  $\text{SiO}_2$ . (It may be noted that while U.S. Patent No. 4 440 871 mentions the possibility of using a tetraalkyl silicate as silicon source, none of its many  
15 examples does so.)

          Although the synthesis mixture is surfactant-free, it is within the scope of the invention to incorporate an organic solvent miscible with water, other than a surfactant, that assists in solubilizing the tetraalkyl  
20 orthosilicate in the aqueous synthesis mixture. As organic solvent there may be mentioned sulphoxides and  $\text{C}_1$  to  $\text{C}_5$  oxygenated hydrocarbons, the latter advantageously being an acid, aldehyde, ketone or mono- or polyhydric alcohol. As examples there may be  
25 mentioned ethylene glycol, 1,2- and 1,3-propanediols, acetone, methanol, n- and isopropanol, butanol and, preferably, ethanol.

          In general, the treatment of the synthesis mixture to yield the desired crystalline molecular sieve,  
30 usually termed hydrothermal treatment, is advantageously carried out under autogenous pressure, for example in an autoclave, for example a stainless

steel autoclave which may, if desired, be ptfe-lined. The treatment may, for example, be carried out at a temperature within the range of from 50, advantageously from 90, especially 120, to 250°C, depending on the molecular sieve being made. The treatment may, for example, be carried out for a period within the range of from 1 to 200 hours, preferably up to 100 hours, again depending on the molecular sieve being formed. The procedure may include an ageing period, either at room temperature or, preferably, at a moderately elevated temperature, before the hydrothermal treatment at more elevated temperature. The latter may include a period of gradual or stepwise variation in temperature.

As source for the phosphorus in the synthesis mixture, there may be mentioned phosphoric acid, organic phosphates, e.g., triethylphosphate, and aluminophosphates.

As source for aluminium in the synthesis mixture there may be mentioned alumina hydrate, alumina, sodium aluminate, pseudoboehmite, aluminium phosphate, organic aluminium sources, e.g., alkoxides, for example, aluminium isopropoxide.

As source for silicon there may be mentioned, as indicated above, a tetraalkyl orthosilicate. There may be used, for example, tetramethyl orthosilicate, tetraethyl orthosilicate, tetrapropyl orthosilicate, and tetrabutyl orthosilicate. Tetraethyl orthosilicate (TEOS) is preferred.

In addition, the synthesis mixture will contain an organic structure-directing agent (template). In general, as indicated above, these compounds are generally organic bases, especially amines and

quaternary ammonium compounds, used either singly or in mixtures.

As templates there may be mentioned, for example, tetraethyl ammonium hydroxide (TEAOH) and salts, e.g., phosphate, fluoride, chloride, bromide and acetate, dipropylamine (DPA), triethylamine, cyclohexylamine, 1-methylimidazole, morpholine, pyridine, piperidine, and diethylethanolamine (DEA).

The treatment may be carried out with the vessel static or, preferably, with stirring or with rotating the vessel about a horizontal axis (tumbling). If desired, the synthesis mixture may be stirred or tumbled during an initial part of the heating stage, for example, from room temperature to an elevated, e.g., the final treatment, temperature, and be static for the remainder. Agitation generally produces a product with a smaller particle size and a narrower particle size distribution than static hydrothermal treatment.

A synthesis mixture for producing SAPO-34 according to the invention advantageously has a molar composition, within the following ranges:

$P_2O_5 : Al_2O_3$       0.6 to 1.2 : 1,

preferably      about 1 : 1

$SiO_2 : Al_2O_3$       0.01 to 0.5 : 1,

preferably      0.1 to 0.5 : 1

$H_2O : Al_2O_3$       10 to 100 : 1

together with an organic template, advantageously tetraethylammonium hydroxide (TEAOH), dipropylamine

(DPA), isopropylamine or morpholine, or a mixture of two or more such templates, in a proportion appropriate to yield SAPO-34.

The present invention also provides the use in the manufacture of SAPO-34 by hydrothermal treatment of a synthesis mixture comprising sources of silicon, aluminium and phosphorus, of a tetraalkyl orthosilicate as silicon source to control the particle size of the product.

The invention further provides the products of the processes and of the uses of the earlier aspects of the invention. The products, if required after cation exchange and/or calcining, have utility as catalyst precursors, catalysts, and separation and absorption media.

The molecular sieves of the present invention can be used as seeds in the manufacture of molecular sieves. The molecular sieves prepared by the method of the present invention may be used to seed the formation of molecular sieves of the same structure type or of a different structure type. They can be used to seed the formation of a zeolite or of a phosphorus-containing molecular sieve. The seeding of a phosphorus-containing synthesis mixture is described in above-mentioned International application WO 00/06493, the disclosure of which is incorporated herein by reference.

As used in this specification, the term "structure type" is used in the sense described in the Structure Type Atlas, Zeolites 17, 1996.

Accordingly, the present invention also relates to a process for manufacturing a molecular sieve, comprising (i) forming a synthesis mixture from a



crystalline silicoaluminophosphate molecular sieve of the invention, sources of aluminium and of silicon, optionally a source of phosphorus and optionally one or several structure-directing agents (templates) and any other material necessary to form the molecular sieve, and (ii) treating the synthesis mixture for a period and at a temperature appropriate for the manufacture of the molecular sieve.

In the embodiment where the silicoaluminophosphate molecular sieve of the invention is used as a seed, it is generally present in the synthesis mixture in a concentration of up to 10000 ppm, advantageously at most 3000 ppm, more advantageously at most 1500 ppm, and preferably at most 1000 ppm, more preferably at most 500 ppm, and most preferably at most 350 ppm, based on the total weight of the synthesis mixture. A minimum seeding level is generally 1 ppb (0.001 ppm), advantageously at least 0.1 ppm, more advantageously at least 1 ppm, and preferably at least 10 ppm, based on the total weight of the synthesis mixture. Advantageous ranges of proportions are from 1 ppm to 2000 ppm, preferably from 100 ppm to 1500 ppm, and most preferably from 100 ppm to 250 ppm.

The seeds are advantageously incorporated in the synthesis mixture in the form of a suspension, preferably a colloidal suspension, advantageously in an aqueous medium, preferably water, or another liquid component of the synthesis mixture. As used herein, the term "colloidal", when used of a suspension, refers to one containing discrete finely divided particles, dispersed in a continuous liquid phase and preferably refers to a suspension that is stable, in the sense

that no visible separation occurs or sediment forms, in a period sufficient for the use intended, advantageously for at least 10 hours, more advantageously at least 20 hours, preferably at least 100 hours, and more preferably at least 500 hours, at ambient temperature (23°C).

When the silicoaluminophosphate molecular sieves of the invention are used as seeds, they have a mean particle size of at most 400 nm, advantageously at most 200 nm, preferably at most 100 nm, and most preferably at most 50 nm.

In another embodiment, the silicoaluminophosphate molecular sieve of the invention are especially useful in numerous hydrocarbon conversions, separations and absorptions. They may be used alone, or in admixture with other molecular sieves, in particulate form, supported or unsupported, or in the form of a supported layer, for example in the form of a membrane, for example as described in International Application WO 94/25151. Hydrocarbon conversions include, for example, cracking, reforming, hydrofining, aromatization, oligomerisation, isomerization, dewaxing, and hydrocracking (e.g., naphtha to light olefins, higher to lower molecular weight hydrocarbons, alkylation, transalkylation, disproportionation or isomerization of aromatics). Other conversions include the reaction of alcohols with olefins and the conversion of oxygenates to hydrocarbons, especially of methanol to olefins, especially light olefins. SAPO-34 produced by the process of the invention is especially suitable for this conversion.

Conversion of oxygenates may be carried out with the oxygenate, e.g., methanol, in the liquid or, preferably, the vapour phase, in batch or, preferably, continuous mode. When carried out in continuous mode, a weight hourly space velocity (WHSV), based on oxygenate, of advantageously 1 to 1000, preferably 1 to 100, hour<sup>-1</sup> may conveniently be used. An elevated temperature is generally required to obtain economic conversion rates, e.g., one between 300 and 600°C, preferably from 400 to 500°C, and more preferably about 450°C. The catalyst may be in a fixed bed, or a dynamic, e.g., fluidized or moving, bed.

The oxygenate feedstock may be mixed with a diluent, inert under the reaction conditions, e.g., argon, nitrogen, carbon dioxide, hydrogen, or steam. The concentration of methanol in the feedstream may vary widely, e.g., from 5 to 90 mole per cent of the feedstock. The pressure may vary within a wide range, e.g., from atmospheric to 500 kPa.

The following Examples, in which parts are by weight unless otherwise indicated, illustrate the invention. The source and purity of starting materials are those first given, unless indicated otherwise.

#### Example 1

This example illustrates the manufacture of SAPO-34 using the process of the invention.

A synthesis mixture was prepared as follows:

9.75 parts of H<sub>3</sub>PO<sub>4</sub> (85%), 9.70 parts of deionized water, and 5.84 parts of alumina hydrate (Catapal, Vista, 74% Al<sub>2</sub>O<sub>3</sub>, 26% H<sub>2</sub>O) were mixed together. Then 35.6 parts of TEAOH (35% in water) were added and mixed

in. Finally 15.6 parts of ethanol and 3.5 parts of TEOS were mixed in, to yield a synthesis mixture of molar composition:

5             $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.4 \text{ SiO}_2 : 2 \text{ TEAOH} : 50 \text{ H}_2\text{O} : 8$   
             $\text{C}_2\text{H}_5\text{OH}$

10            The synthesis mixture was placed in a ptfe-lined stainless steel autoclave, which was mounted on a shelf in an air oven, the shelf being rotated, tumbling the autoclave, and maintained at 200°C for 24 hours. After cooling, the product was recovered by centrifuging, washed with water, and dried in an air oven. The powder X-ray diffraction (XRD) pattern showed the  
15            product to be SAPO-34 with some minor SAPO-18 intergrowth. The relatively broad diffraction peaks indicated a small crystal size.

20            Elemental analysis : Si, 3.72% : Al, 17.67%; P, 16.85%, representing a product stoichiometry of  $\text{Si}_{0.100} \text{Al}_{0.492} \text{P}_{0.409}$ .

25            Analysis of the peak widths of the XRD pattern and application of the Scherrer equation, correcting for the peak broadening caused by the instrument and the intergrowths, gave a mean crystal size of about 50nm.

#### Example 2

            In a procedure similar to that of Example 1, a synthesis mixture was prepared of molar composition:

30             $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.3 \text{ SiO}_2 : 2 \text{ TEAOH} : 40 \text{ H}_2\text{O} : 8$   
             $\text{C}_2\text{H}_5\text{OH}$

The synthesis mixture was placed in a ptfe-lined stainless steel autoclave, mounted on a shelf in an air oven, the shelf being rotated, and maintained at 200°C for 24.5 hours. Recovery was carried out as in Example 1. The product was SAPO-34 with some minor SAPO-18 intergrowth. SEM analysis showed crystal size to be less than 0.1  $\mu\text{m}$ , and analysis of the XRD pattern peak width and use of the Scherrer equation gave a mean crystal size of about 36 nm.

Elemental analysis : Si, 3.40%; Al, 17.4%; P, 16.4%

Stoichiometry  $\text{Si}_{0.093} \text{Al}_{0.498} \text{P}_{0.409}$

### Example 3

Following the procedure of Example 1, there was prepared a synthesis mixture of molar composition:

$\text{Al}_2\text{O}_3$  :  $\text{P}_2\text{O}_5$  : 0.3  $\text{SiO}_2$  : 1.52 TEAOH : 30  $\text{H}_2\text{O}$  : 16  $\text{C}_2\text{H}_5\text{OH}$

Hydrothermal treatment (200°C, 24.5 hours) and recovery were carried out as described in Example 2. The product was SAPO-34 with some minor SAPO-18 intergrowth. The relatively large width of the XRD pattern peaks indicated small crystal size, SEM analysis indicated a mean particle size of about 0.1  $\mu\text{m}$ .

Elemental analysis : Si, 3.51%; Al, 17.4%; P 16.5%

Stoichiometry :  $\text{Si}_{0.096} \text{Al}_{0.495} \text{P}_{0.416}$

Example 4

148.9 parts  $\text{Al}_2\text{O}_3$  (Condea Pural SB) were mixed with 590.9 parts of water, and 252.4 parts of  $\text{H}_3\text{PO}_4$  (85%, Acros) together with 69.8 parts of TEOS were then added. 460.5 parts of TEAOH (35% in water, Eastern Chemical) together with 177.3 parts of DPA (Fluka) were then added, with continuous stirring to yield a synthesis mixture of molar composition:



The synthesis mixture was placed in a stainless steel autoclave, heated over the course of 8 hours to 175°C and maintained at that temperature with stirring at 170 rpm (tip speed of 0.89 m/s) for 48 hours. After recovery and analysis, the product was found to be pure SAPO-34. 50% by number of the crystals were of particle size less than 280 nm; 10% were of particle size greater than 400 nm. In comparison, using as silica source Ludox AS40, a 40% colloidal silica solution, instead of TEOS, in a synthesis mixture of the same molar composition and the same reaction conditions gave a pure SAPO-34 product of particle size about 1  $\mu\text{m}$ .

Example 5

19.8 parts of  $\text{H}_3\text{PO}_4$  (85%), 30 parts water, 5.4 parts TEOS, 11.9 parts alumina hydrate (Catapal), 72.3 parts TEAOH (35%), and 20.7 parts water were mixed in the order stated to give a synthesis mixture of the following molecular proportions:

$\text{Al}_2\text{O}_3$  :  $\text{P}_2\text{O}_5$  : 0.3  $\text{SiO}_2$  : 2 TEAOH : 70  $\text{H}_2\text{O}$

5 After homogenization in a blender, the synthesis  
mixture was placed in a ptfe-lined stainless steel  
autoclave, mounted for tumbling in an oven, and  
maintained at 200°C for 24 hours. After cooling, the  
product was recovered by centrifuging, washed with  
water, and dried at 115°C. The XRD pattern showed the  
10 product to be pure SAPO-34, SEM showing cubic and thick  
platelet crystals of size ranging between 50 and 200  
nm.

CLAIMS:

1. A process for the manufacture of a SAPO-34  
crystalline molecular sieve, the process  
5 comprising: (a) forming a surfactant-free synthesis  
mixture containing sources of silicon, of  
aluminium, and of phosphorus, in proportions  
appropriate to the formation of SAPO-34, and a  
structure-directing agent, the source of silicon  
10 being a tetraalkyl orthosilicate, and (b)  
subjecting the synthesis mixture to hydrothermal  
treatment.
2. A process as claimed in claim 1 wherein the molar  
15 ratio of silicon to aluminium, expressed as  $\text{SiO}_2$  :  
 $\text{Al}_2\text{O}_3$ , is at most 0.5:1.
3. A process as claimed in claim 1 or claim 2,  
wherein the tetraalkyl orthosilicate is tetraethyl  
20 orthosilicate.
4. A process as claimed in claim 1 or claim 2,  
wherein the tetraalkyl orthosilicate is  
tetramethyl orthosilicate, tetrapropyl  
25 orthosilicate, tetrabutyl orthosilicate, or a  
mixture thereof.
5. A process as claimed in any one of claims 1 to 4,  
wherein the structure-directing agent is TEAOH or  
30 a mixture of TEAOH and DPA.



6. A process as claimed in any one of claims 1 to 5, wherein at least a part of the hydrothermal treatment step is carried out with agitation.

5 7. A process as claimed in any one of claims 1 to 6, wherein the synthesis mixture has a molar composition within the ranges of

P <sub>2</sub> O <sub>5</sub>	:	Al <sub>2</sub> O <sub>3</sub>	0.6:1 to 1.2:1
SiO <sub>2</sub>	:	Al <sub>2</sub> O <sub>3</sub>	0.01:1 to 0.5:1
H <sub>2</sub> O	:	Al <sub>2</sub> O <sub>3</sub>	10:1 to 100:1

10 together with a structure-directing agent.

15 8. A SAPO-34 crystalline molecular sieve whenever produced by a process as claimed in any one of claims 1 to 7.

9. A SAPO-34 crystalline molecular sieve the mean particle of which is at most 400 nm.

20 10. A SAPO-34 crystalline molecular sieve the mean particle of which is at most 200 nm.

25 11. A SAPO-34 crystalline molecular sieve the mean particle of which is at most 100 nm.

12. A SAPO-34 crystalline molecular sieve the mean particle of which is at most 50 nm.

30 13. The use, in the manufacture of a SAPO-34 by hydrothermal treatment of a synthesis mixture comprising sources of silicon, aluminum, and

phosphorus, of a tetraalkyl orthosilicate as silicon source to control the particle size of the product.

- 5      14. The use as claimed in claim 13, wherein the synthesis mixture is surfactant-free.
15. The use as claimed in claim 13 or claim 14 wherein the molar ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  is at most 0.5:1.
- 10      16. A process for the conversion of an oxygenate to olefins which comprises contacting the oxygenate under catalytic conversion conditions with a molecular sieve as claimed in any one of claims 8 to 12.
- 15      17. The use of the molecular sieve as claimed in any one of claims 8 to 12, if desired after washing, cation exchange, or calcining, in hydrocarbon conversion, adsorption, or separation.
- 20      18. The use of the molecular sieve as claimed in any one of claims 8 to 12, if desired after washing, cation exchange, or calcining, in converting an oxygenate to olefins.
- 25      19. A process for manufacturing a molecular sieve, comprising (i) forming a synthesis mixture from a SAPO-34 crystalline molecular sieve as claimed in one of claims 8 to 12, sources of aluminium and of silicon, optionally a source of phosphorus and optionally one or several structure-directing
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agents (templates) and any other material  
necessary to form the molecular sieve, and (ii)  
treating the synthesis mixture for a period and at  
a temperature appropriate for the manufacture of  
the molecular sieve.

5

20. The use, in the manufacture of a crystalline  
molecular sieve by hydrothermal treatment of a  
synthesis mixture containing sources of silicon  
and of aluminium, and optionally of phosphorus, of  
providing a SAPO-34 crystalline molecular sieve as  
claimed in any one of claims 8 to 12 as seed to  
help forming the crystalline molecular sieve.

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## INTERNATIONAL SEARCH REPORT

International Application No

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B37/08 B01J29/04 C07C1/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 440 871 A (MESSINA CELESTE A ET AL) 3 April 1984 (1984-04-03) cited in the application claims 1,8,30,35-38 column 8, line 3-9	8
A	examples 32-38; table XII	13-18
X	DAHL I M ET AL: "The effect of crystallite size on the activity and selectivity of the reaction of ethanol and 2-propanol over SAPO-34" MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 29, no. 1-2, June 1999 (1999-06), pages 159-171, XP004167557 ISSN: 1387-1811	8-12, 16-18
A	page 159-164; figure 3; tables 1,2 --- -/-	1-8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

3 February 2003

Date of mailing of the international search report

21/02/2003

Name and mailing address of the ISA

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Authorized officer

Rhodes, K

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 02/26205

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 36328 A (EXXON CHEMICAL PATENTS INC) 25 May 2001 (2001-05-25) cited in the application claims 1,3-6,10-13 page 2, line 27 -page 3, line 13 page 6, line 14-25 page 7, line 21-31 page 8, line 22,23	13
A	examples 1-3	1-15,19, 20
X	----- WO 00 06493 A (JANSSEN MARCEL J G ;MERTENS MACHTELD M (BE); MORTIER WILFRIED J (B) 10 February 2000 (2000-02-10) cited in the application claims 1-4,9,13-19,22-24 page 2, line 1-19 page 6, line 1-23 page 8, line 9-25	8,19,20
A	page 9, line 20 -page 10, line 3 examples 3,10	1-20
X	----- LI ZU-GUANG ET AL: "Synthesis and properties of SAPO-34 catalyst for endothermic fuel" TUIJIN JISHU;TUIJIN JISHU/JOURNAL OF PROPULSION TECHNOLOGY AUGUST 2001, vol. 22, no. 4, August 2001 (2001-08), pages 341-344, XP009005107	16-18
X	& DATABASE COMPENDEX 'Online! ENGINEERING INFORMATION, INC., NEW YORK, NY, US; LI ZU-GUANG ET AL.: "Synthesis and properties of SAPO-34 catalyst for endothermic fuel." Database accession number: E2002206947186 abstract	16-18
A	----- ANJANA BHATTACHARYA ET AL: "STUDIES ON THE SYNTHESIS OF SAPO-5" JOURNAL OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY. (INTERNATIONAL JOURNAL OF BIOTECHNICAL AND CHEMICAL PROCESSES), ELSEVIER APPLIED SCIENCE PUBLISHERS. BARKING, GB, vol. 54, no. 4, 1992, pages 399-407, XP000301502 ISSN: 0268-2575 Preparation of materials (p. 400); Effect of silica source (p. 403) table 1	1-8
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/26205

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-20

1.1. Claims: 1-8,16-20

1.2. Claims: 9,16-20

1.3. Claims: 10,16-20

1.4. Claims: 11,16-20

1.5. Claims: 12,16-20

1.6. Claims: 13-15

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/26205

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4440871	A	03-04-1984	AT 22272 T	15-10-1986
			CA 1202016 A1	18-03-1986
			DE 3366290 D1	23-10-1986
			DK 339883 A	27-01-1984
			EP 0103117 A1	21-03-1984
			ES 8504077 A1	01-07-1985
			ES 8604783 A1	01-08-1986
			ES 8602094 A1	01-03-1986
			JP 1703764 C	14-10-1992
			JP 3072010 B	15-11-1991
			JP 59035018 A	25-02-1984
			NO 832712 A ,B,	27-01-1984
			US 5114563 A	19-05-1992
WO 0136328	A	25-05-2001	AU 1359901 A	30-05-2001
			AU 1460501 A	30-05-2001
			CN 1391532 T	15-01-2003
			EP 1233928 A1	28-08-2002
			NO 20022209 A	08-05-2002
			WO 0136328 A1	25-05-2001
			WO 0136329 A1	25-05-2001
WO 0006493	A	10-02-2000	AU 5177399 A	21-02-2000
			AU 750576 B2	25-07-2002
			AU 5178299 A	21-02-2000
			BR 9912472 A	17-04-2001
			CA 2337505 A1	10-02-2000
			CA 2337628 A1	10-02-2000
			CN 1311758 T	05-09-2001
			CN 1311757 T	05-09-2001
			EP 1105348 A1	13-06-2001
			EP 1105347 A1	13-06-2001
			WO 0006494 A1	10-02-2000
			WO 0006493 A1	10-02-2000
			JP 2002521303 T	16-07-2002
			JP 2002521304 T	16-07-2002
			NO 20010463 A	28-03-2001
			AU 5176799 A	21-02-2000
			CA 2337506 A1	10-02-2000
			EP 1105346 A1	13-06-2001
			WO 0006492 A1	10-02-2000